

## Research progress of low-temperature SCR denitration catalysts

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**Abstract:** Nitrogen oxide  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ ) is one of the major pollutants in the air pollution, it can cause environmental problems such as photochemical smog, acid rain, and ozone layer destruction, which has posed threat to people's living environment and quality of life, and attracted great attention from the world. Countries made stricter emission standards for burning emissions from both fixed and mobile sources. The major denitrification technologies include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), oxidative denitrification, and activated carbon adsorption and denitrification at present. The SNCR has higher conditions in industrial applications, the main factors affecting successful operation are temperature, ammonia–nitrogen ratio, distribution of ammonia gas in the flue gas and residence time, so there were certain limitations in industrial application of SNCR. Compared with other denitrification technologies, SCR denitration technology is more widely used in industrial application, in which denitration is mostly arranged after dust removal and desulfurization, at this time, the temperature is mostly between 100~250 °C. The performance of SCR denitrification in low-temperature must be improved, which is one of the most promising flue gas  $\text{DeNO}_x$  technology. In this paper, the recent works on low-temperature SCR catalysts were reviewed on manganese-based catalysts, vanadium-based catalysts and carbon-based catalysts. Single-component Mn-based catalysts, supported Mn-based catalysts and composite Mn-based catalysts were reviewed, the effects of preparation of V-based catalysts on the de-dumping and denitrification mechanisms were described. The effect of transition metal doping on C-based catalysts was reviewed. The influence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  resistance on low-temperature  $\text{NH}_3$ -SCR catalytic activity and reaction mechanism were also discussed. Finally, the virtues advantages and defects of low temperature SCR catalysts were summarized, and the future development direction was also given out.

### Key learning points:

- (1) Catalysts for different systems were reviewed. The problems of manganese-based catalysts, vanadium-based catalysts and carbon-based catalysts were analyzed. The preparation methods were used to improve the water and sulfur resistance and catalytic activity of the catalysts.
- (2) Denitrification mechanism. From the currently reported denitration mechanism to analyze the activity of the catalyst, it is expected that the mechanism rsearches will improve the low temperature performance of the catalyst.
- (3) Water and sulfur resistance of low temperature catalyst. The presence of  $\text{SO}_2$  at low temperatures tends to result in ABS deposition.

**Key words:** low-temperature; selective catalytic reduction; denitrification; catalyst; mechanism

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# 低温 SCR 脱硝催化剂研究进展

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**摘 要:** 氮氧化物  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$  和  $\text{N}_2\text{O}$ ) 是全球大气污染的主要污染物之一, 引起光化学烟雾、酸雨、臭氧层破坏等环境问题, 严重影响人们的生存环境和生活质量, 引起了世界各国的广泛关注。针对固定源和移动源燃烧排放, 各国制定了日益严格的排放标准。目前主要的脱硝技术分为选择性催化还原 (SCR)、选择性非催化还原 (SNCR)、氧化脱硝和活性炭吸附脱硝等。SNCR 的应用有较高的条件, 影响其成功运行的主要因素有温度、氨氮比、氨气在烟气中的分布和停留时间等, 故 SNCR 的工业应用存在一定的局限性。SCR 脱硝技术比其它脱硝技术应用更广泛, 其中脱硝多安排于除尘脱硫后, 此时温度多处于  $100\sim 250\text{ }^\circ\text{C}$  之间。为提高 SCR 脱硝性能, 低温 SCR 脱除  $\text{NO}_x$  是目前研究最热门的烟气脱硝技术。本工作综述了近年来低温 SCR 脱硝催化剂的研究进展, 介绍了锰基催化剂、钒基催化剂及碳基催化剂的发展现状, 对单组分 Mn 基催化剂、负载型 Mn 基催化剂和复合型 Mn 基催化剂进行了综述, 从 V 基催化剂的制备对脱硝的影响和脱硝机理进行了表述, 综述了过渡金属掺杂对 C 基催化剂的影响, 阐述了烟气中  $\text{H}_2\text{O}$  和  $\text{SO}_2$  对催化反应的影响及低温 SCR 反应的脱硝机理, 对低温 SCR 催化剂进行了总结并对其未来发展进行了展望。

**要 点:**

- (1) 综述了不同体系的催化剂, 分析了锰基催化剂、钒基催化剂和碳基催化剂各自存在的问题, 通过掺杂改性, 从制备方法上提高催化剂的耐水耐硫性能和催化活性。
- (2) 从目前报道的脱硝机理分析催化剂活性和催化机理入手有望提高催化剂的低温性能。
- (3) 低温催化剂耐水耐硫, 低温下  $\text{SO}_2$  存在易导致硫酸铵盐沉积。

**关键词:** 低温; 选择性催化还原; 脱硝; 催化剂; 机理

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## 1 INTRODUCTION

Nowadays,  $\text{NO}_x$  has become one of the main pollutants in the atmospheric environment which can lead to photochemical smog and acid rain. Selective catalytic reduction (SCR) denitration is the most commonly used technology of denitration.  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$  catalyst is widely used because of its excellent denitration performance with water and sulfur resistance. Its reaction temperature range is  $300\sim 400\text{ }^\circ\text{C}$ <sup>[1,2]</sup>, and denitration devices are usually set up between the economizer and the dust collector in order to ensure the activity of the catalyst. However, large amount of  $\text{SO}_2$ , dust and alkali in flue gas are harmful to the catalyst service life. In recent years, emissions standards become increasing strict. Many flue gases such as coke oven flue gas, the ore sintering flue gas, and waste incineration flue gas do not have the appropriate temperature range ( $300\sim 400\text{ }^\circ\text{C}$ ) for regular SCR process. Their flue gas temperatures are commonly below  $300\text{ }^\circ\text{C}$ <sup>[3,4]</sup>, which are not the ideal catalytic temperature

for the mature catalyst at present. Accordingly, low temperature SCR denitration technology is greatly developed.

Low temperature SCR denitration technology still maintained higher activity under  $300\text{ }^\circ\text{C}$ . The denitration device is set up behind the dust removal and desulfurization device, and high concentration of  $\text{SO}_2$ , alkali and dust could be avoided<sup>[5]</sup>. Recently, increasing attention has been devoted to the low temperature catalysts. In this article, the catalysts were summarized, and  $\text{H}_2\text{O}$  and  $\text{SO}_2$  in flue gas on the influence of catalytic activity and reaction mechanism were also discussed.

## 2 LOW TEMPERATURE SCR CATALYST

### 2.1 Manganese-based Catalysts

The low-temperature SCR catalyst has a higher denitration activity because of its wide variation of valence state, which promotes  $\text{NH}_3$  to selective reduction of  $\text{NO}_x$ . The manganese-based catalysts have showed increasing importance due to their high efficiency. In

previous studies, single component manganese-based catalysts, supported manganese-based catalysts, and composite manganese-based catalysts were developed.

### 2.1.1 Single component manganese-based catalysts

Tian et al.<sup>[6]</sup> prepared  $\text{MnO}_2$  with different morphologies using different methods (Fig.1). The experimental results showed that nanorods  $\text{MnO}_2$  contributed the best denitrification effect (Table 1). High activity of the rod-like  $\text{MnO}_2$  was due to the large amount

of strong acid sites, low crystallinity and more lattice oxygen. Tang et al.<sup>[7]</sup> synthesized  $\text{MnO}_2$  catalysts with different methods. It was found that  $\text{MnO}_2$  prepared by solid phase method and rheological method exhibited excellent low temperature activity, and the conversion rate of  $\text{NO}_x$  at  $100^\circ\text{C}$  was close to 100%. At the same time, the analysis showed that the amorphous state of the catalyst was the key factor for the low temperature catalytic activity.

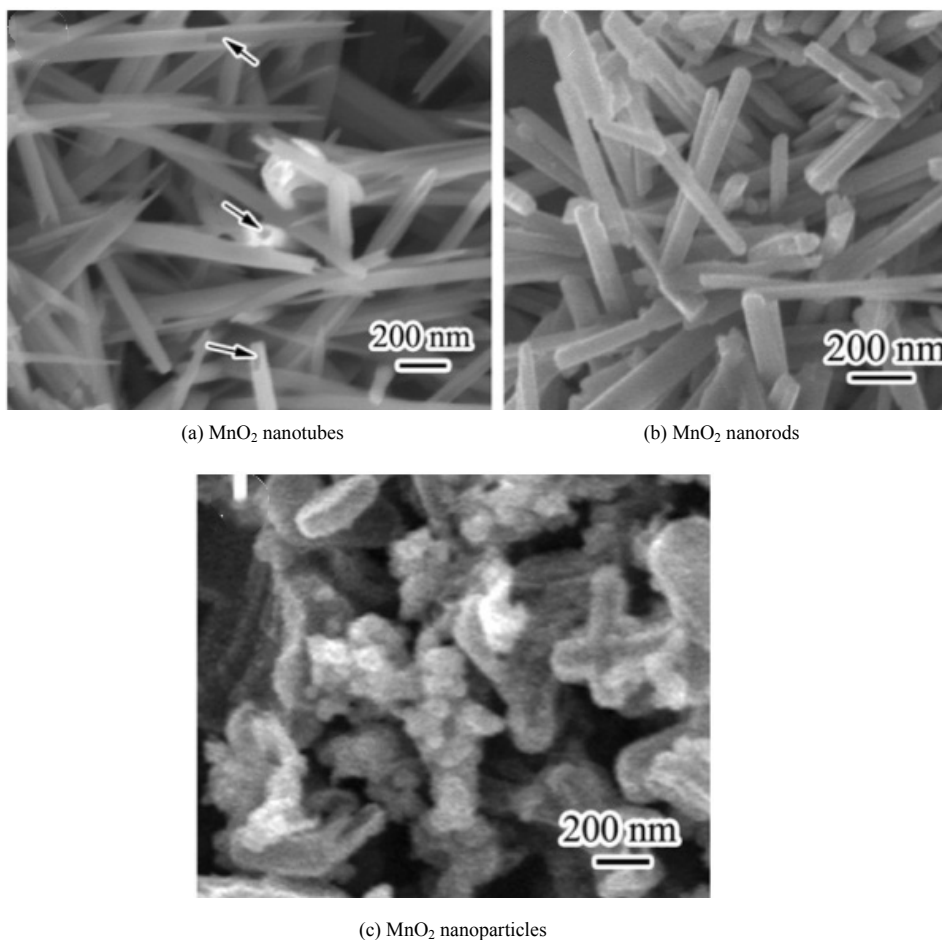


Fig.1 SEM images of the  $\text{MnO}_2$ <sup>[6]</sup>

**Table 1 Catalytic reduction of  $\text{NO}_x$  over different-shaped  $\text{MnO}_2$**

$\text{MnO}_2$ morphology	Temperature/ $^\circ\text{C}$	$\text{NO}_x$ conversion rate/%
Nanotubes	300	60.8
Nanoparticles	300	78.5
Nanorods	300	98.2

### 2.1.2 Supported manganese-based catalysts

Supported manganese-based catalysts were summarized in Table 2. Wu et al.<sup>[8]</sup> prepared a series of Ce-modified CeMnTi catalysts and evaluated the activity of catalysts with different Ce contents. The results were

showed in Fig.2. It can be seen that the addition of Ce can improve the activity of the catalyst. When the Ce content was 0.07%, the catalyst contributed the highest catalytic activity. When the temperature rose to  $120^\circ\text{C}$ , the denitration efficiency was 100% at  $40000\text{ h}^{-1}$  space velocity. For the sample without Ce addition,  $\text{NO}$  conversion rate was 71% under the same reaction conditions. Through the analysis of TPR and XPS, it was found that Ce modification increased the chemical adsorption ability of oxygen and acidic sites on the

surface of the catalyst, which were beneficial to the catalytic reaction.

**Table 2 Catalytic reduction of NO<sub>x</sub> over Mn-based catalysts**

Catalyst	Temperature/°C	NO concentration/ $\times 10^{-6}$ , vol	Conversion rate/%	Reference
10% MnO <sub>x</sub> /TiO <sub>2</sub>	210	800	100	[8]
0.07% CeMnTi	120	1000	100	[9]
5% Mn–2% Ni/TiO <sub>2</sub>	200	400	100	[10]
Mn–0.4% Ni/TiO <sub>2</sub>	200	400	100	[11]
0.1% Fe–Mn–Ce/TiO <sub>2</sub>	200	600	100	[12]
5% $\gamma$ -MnO <sub>2</sub> /TiO <sub>2</sub> –Palygorskite	200	1000	100	[13]
30% Mn–Fe/SiO <sub>2</sub>	160	1000	99.1	[14]
4% Ce–MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	250	1000	98	[15]

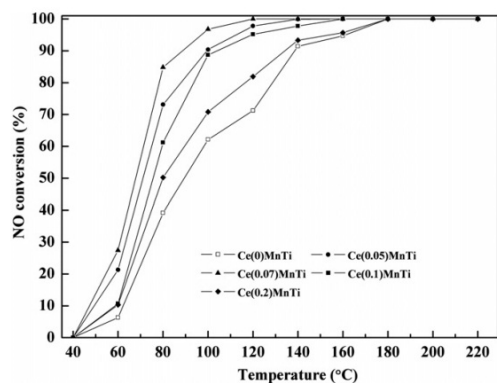


Fig.2 NO conversion rate of Ce modified MnO<sub>x</sub>/TiO<sub>2</sub> catalysts at different temperatures<sup>[8]</sup>

Thirupath et al.<sup>[9,10]</sup> doped Ni to MnO<sub>x</sub>/TiO<sub>2</sub> catalyst. The results showed that Ni doping improved the denitrification efficiency. The presence of Ni enhanced the stability of active Mn<sup>4+</sup> in the catalyst, and inhibits the formation of Mn<sup>3+</sup>, and improved the H<sub>2</sub>O and SO<sub>2</sub> resistance. Shen et al.<sup>[11]</sup> doped Fe in Mn–Ce/TiO<sub>2</sub>, and the catalyst showed good activity when the molar ratio of Fe/Ti was 0.1. The addition of Fe also improved the resistance ability of H<sub>2</sub>O and SO<sub>2</sub> for the catalyst, and resistance ability was strengthened with the increase of Fe content until Fe content was 0.15%. Luo et al.<sup>[12]</sup> loaded MnO<sub>2</sub> with different crystallines on TiO<sub>2</sub>–palygorskite (TiO<sub>2</sub>–Pal), and found that  $\gamma$ -MnO<sub>2</sub> gave higher activity than  $\delta$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>. MnO<sub>2</sub> particles had a better dispersion in the carrier when mass ratio of Pal to TiO<sub>2</sub> was 2:1. Huang et al.<sup>[13]</sup> loaded Mn and Fe oxides onto mesoporous SiO<sub>2</sub> with Mn/Fe mass ratio of 1 and calcination temperature at 400 °C, and 99.1% NO conversion rate was achieved at 160 °C, and H<sub>2</sub>O has little effect on the catalytic activity. Guo et al.<sup>[14]</sup> prepared Ce–MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts using impregnation method. The denitrification performance of the catalysts in the range of 70–300 °C was investigated. The results

showed that Ce addition can improve the dispersion of MnO<sub>x</sub> on the carrier surface. 4% Ce–MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> showed good denitrification efficiency. The effect of calcination temperature on the catalytic performance was also investigated, and it found that the catalyst calcined at 550 °C contributed the best catalytic performance. Zhang et al.<sup>[16]</sup> prepared MnO<sub>x</sub>/TiO<sub>2</sub> catalysts using conventional impregnation method, ultrasonic impregnation method and sol–gel method, and employed them in SCR reactions. The results revealed that the catalyst obtained by ultrasonic impregnation gave the best catalytic activity at low temperature. The conversion rate of NO was more than 90% at 120 °C. The other two catalysts gave comparable denitrification efficiency almost at 150 °C. The results illustrated that the sample using ultrasonic impregnation method exhibited higher dispersibility for active species, and more Lewis acid sites, which improved the catalytic performance.

### 2.1.3 Composite manganese-based catalysts

With the development of low temperature SCR catalyst, complex transition metal oxidation catalyst has been thoroughly studied. Among these catalysts, the composite Mn-based catalysts were of great importance because of its wide reaction temperature range and higher denitrification efficiency. The composite Mn-based catalysts and their denitrification performance were listed in Table 3. Li et al.<sup>[15]</sup> prepared MnFeO<sub>x</sub> nanorods used a hydrothermal method and their NO<sub>x</sub> conversion rates at different temperatures were evaluated, the results indicated that the MnFe<sub>0.1</sub>O<sub>x</sub> nanorods exhibited the highest NO conversion rate in NH<sub>3</sub>-SCR reaction. The SCR activities of MnFeO<sub>x</sub> nanorods with different Fe/Mn molar ratios were presented, the pure MnO<sub>2</sub> nanorods and traditional V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> catalyst were also investigated for comparison. It was found that SCR

activity of  $V_2O_5-WO_3/TiO_2$  catalyst was only less than 20% below 150 °C. Moreover, pure  $MnO_2$  nanorod samples obtained lower NO removal rate in the studied temperature window. It was obvious that the NO conversion rate of  $MnFe_{0.1}O_x$  nanorods could reach approximately 100% at above 200 °C, which was the best Fe/Mn molar ratio. It was reported that oxidation activity of NO to  $NO_2$  over catalysts played a key role in faster reaction:  $NO + NH_3 + 1/4O_2 \rightarrow N_2 + 3/2H_2O$ . Hence, the conversion of NO to  $NO_2$  in absence of  $NH_3$  on sample was researched [Fig.3(b)]. It can be seen that  $MnFe_{0.1}O_x$  nanorod catalysts obtained higher oxidation activity of NO to  $NO_2$ . It was reported that  $NH_4$  ions reacted with gaseous  $NO_2$  molecules to generate  $NH_4NO_2$ , which was decomposed to  $N_2$  and  $H_2O$  in SCR reaction. Therefore,

it was illustrated that a high oxidation capacity of NO to  $NO_2$  or high  $NO_2$  content resulting in a good SCR catalytic activity as shown in Fig.3. The BET surface area of  $MnFeO_x$  bimetallic oxides catalysts was larger than that of pure  $MnO_2$  nanorods and the BET surface area of the  $MnFe_{0.1}O_x$  nanorod was larger than those of others  $MnFeO_x$  bimetallic oxides catalysts as listed in Table 4. Li et al.<sup>[15]</sup> proposed the reaction mechanism of SCR reaction to remove  $NO_x$  by  $NH_3$ . It was supposed that a redox reaction may occur between Mn and Fe ions resulting in electronic transfer. The electronic transfer played a key role in the oxidation of NO to  $NO_2$  during the  $NH_3$ -SCR reaction of removing  $NO_x$  as shown in Fig.4.

Table 3 Catalytic reduction of  $NO_x$  over mixed Mn-based catalysts

Catalyst	Temperature/°C	NO concentration/ $\times 10^{-6}$ , vol	Conversion rate/%	Reference
$MnFe_{0.1}O_x$	200	500	100	[17]
$MnO_2$	300	500	80	[17]
$Mn_2NbO_x$	125	500	94	[18]
0.5Mn-ZrO <sub>x</sub>	100	1000	100	[19]
0.4Ni-MnO <sub>x</sub>	150	500	100	[20]

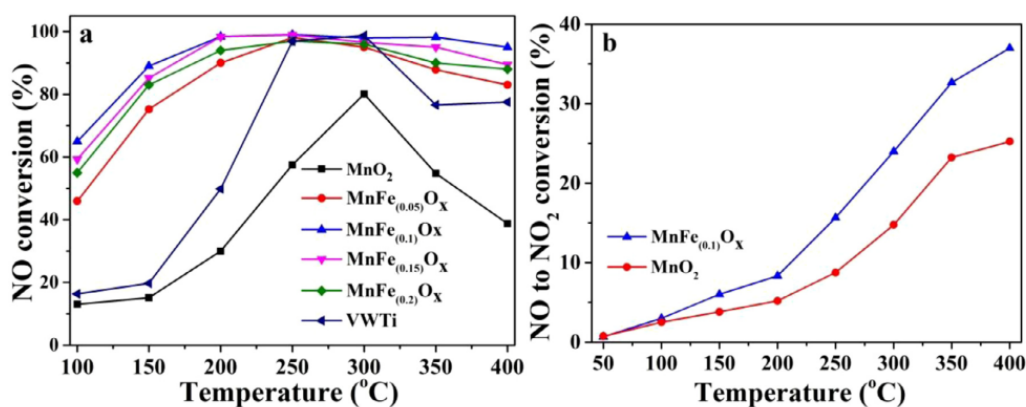


Fig.3 NO conversion rate (a) and conversion of NO to  $NO_2$  (b) over  $MnFeO_x$  nanorods<sup>[15]</sup>

Table 4 Specific area, pore volume and pore diameter distribution of  $MnFeO_x$  nanorods

Material	Specific area/(m <sup>2</sup> /g)	Pore volume/(cm <sup>3</sup> /g)	Pore diameter/nm
$MnO_2$	9.60	0.02	24.78
$MnFe_{0.05}O_x$	22.11	0.07	24.50
$MnFe_{0.1}O_x$	35.32	0.21	16.43
$MnFe_{0.15}O_x$	25.38	0.16	19.80
$MnFe_{0.25}O_x$	25.80	0.12	25.91

Lian et al.<sup>[17]</sup> synthesized a series of Mn-Nb catalysts by homogeneous precipitation, which suggested that the addition of Nb reduced the redox properties of

$MnO_x$ , but increased the Brucellite sites on the catalyst surface, and the low temperature activity of the catalyst was improved. The catalytic performance was the best when the Mn/Nb molar ratio was 2 and the calcination temperature was 500 °C. The NO conversion rate was 94% and the selectivity was 96% at 125 °C. Meanwhile, the  $H_2O$  and  $SO_2$  resistance were improved with Nb addition. Zuo et al.<sup>[18]</sup> prepared Mn-Zr catalyst, and found that  $MnO_x$  was better dispersed when Mn/Zr molar ratio was 0.5, and the catalytic activity was strengthened

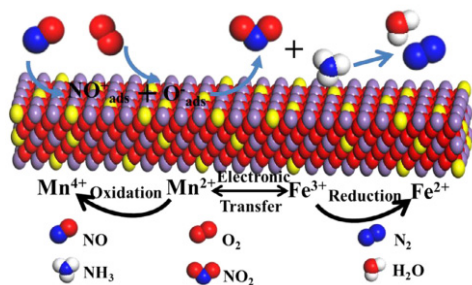


Fig.4 Reaction mechanism of  $\text{NH}_3$ -SCR on  $\text{MnFe}_{0.1}\text{O}_x$  nanorod catalysts<sup>[15]</sup>

due to the synergistic effect between  $\text{Mn}^{n+}$  and  $\text{Zr}^{4+}$ . Liu et al.<sup>[19]</sup> added  $\text{WO}_3$  to the Mn–Zr catalyst. The highly dispersed  $\text{WO}_3$  not only increased the acid sites on the catalyst surface, but also inhibited the adsorption of inert nitrates onto the solid surface, thereby, increasing the utilization of active sites. Wan et al.<sup>[21]</sup> synthesized Ni– $\text{MnO}_x$  catalysts with different molar ratios by co-precipitation. The catalyst showed highest denitrification activity when the molar ratio of Ni/Mn was 0.4. It was illustrated that the catalytic performance was promoted due to the synergistic effect between Ni and Mn.

#### 2.1.4 Summary of manganese-based catalysts

Manganese-based catalysts have high catalytic effect and low temperature range, which have great research space and value in low temperature SCR catalysis research. However, there are a certain amount of  $\text{SO}_2$  and water vapor in various types of flue gas. Manganese-based catalysts exhibit poor denitrification activity when water and  $\text{SO}_2$  coexist. The water and sulfur resistance of the manganese-based catalyst is generally solved from the aspects of preparation method, component doping, and carrier selection. For water and sulfur resistance of manganese-based catalysts, Lin et al.<sup>[20]</sup> reported on the preparation method. An aerosol-assisted spray deposition method was introduced to prepare the Mn–Fe/ $\text{TiO}_2$  catalyst, which shows greatly improved  $\text{NH}_3$ -SCR activity and catalytic tolerance against  $\text{H}_2\text{O}$  and  $\text{SO}_2$  compared to its counterparts prepared by co-precipitation and wet impregnation methods. The spray-synthesized Mn–Fe/ $\text{TiO}_2$  has an improved surface reducibility, which are beneficial for enhancing the SCR activity. Also, the high adsorption ability of  $\text{NH}_3$  and  $\text{NO}_x$  of Mn–Fe/ $\text{TiO}_2$  could also be one

crucial factor determining its superior activity.  $\text{CeO}_2$  has abundant surface oxygen vacancies and strong redox ability. It can effectively store oxygen by redox transition between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ . Therefore, the addition of Ce can effectively improve the oxygen storage capacity of the manganese-based catalyst and promote the oxygen mobility of the catalyst. The addition of Ce can effectively improve the resistance to  $\text{SO}_2$ , prevent the catalyst from being sulfated, and inhibit the formation of ammonium sulfate on the surface of the catalyst<sup>[22,23]</sup>.

## 2.2 Vanadium-based Catalysts

Due to their high activity, high selectivity and good resistant to sulfur and other advantages, V-based catalysts were widely used in the flue gas denitrification for coal, industrial boilers and other emissions.

### 2.2.1 Monometallic vanadium-based catalysts

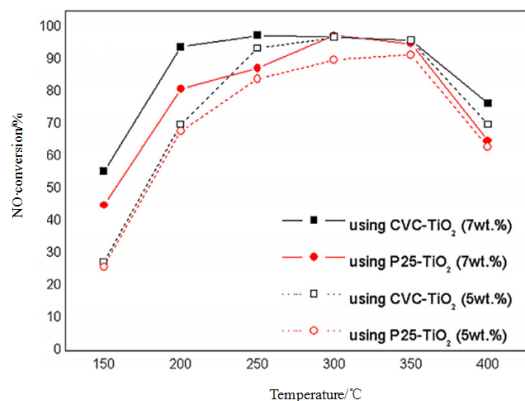
Recently, V-based catalysts have gained increasing importance, and the results were summarized in Table 5. Cha et al.<sup>[24]</sup> prepared  $\text{TiO}_2$  nanoparticles by chemical vapor phase condensation (CVC) method, and then synthesized  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  using the impregnation method.  $\text{V}_2\text{O}_5/\text{P25-TiO}_2$  (a mixed crystal type of  $\text{TiO}_2$ , and the mass ratio of anatase to rutile is about 71/29) was obtained by loading the same amount of  $\text{V}_2\text{O}_5$  on commercial P25- $\text{TiO}_2$ . As shown in Fig.5<sup>[20]</sup>, to achieve the  $\text{NO}_x$  conversion rate of 96%, the required operating temperature of the 7wt%  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  catalyst was about 50 °C lower than that of the 5wt%  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  catalyst. At 200 °C, the  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  catalysts with varying concentrations of  $\text{V}_2\text{O}_5$  showed sufficient  $\text{NO}_x$  conversion, while the  $\text{NO}_x$  conversion efficiencies of the  $\text{V}_2\text{O}_5/\text{P25-TiO}_2$  catalysts with the same  $\text{V}_2\text{O}_5$  concentrations were insufficient. It was proposed that the  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  catalysts had more anatase phase  $\text{TiO}_2$ , a higher specific surface area, and better dispersion than the  $\text{V}_2\text{O}_5/\text{P25-TiO}_2$  catalysts. The characterizations revealed that  $\text{V}_2\text{O}_5/\text{CVC-TiO}_2$  exhibited larger specific surface area, higher dispersion, and more surface oxygen.

Boningari et al.<sup>[25]</sup> prepared V/ $\text{TiO}_2$ , V/ $\text{ZrO}_2$ , V/ $\text{Al}_2\text{O}_3$ , V/ $\text{CeO}_2\text{--Al}_2\text{O}_3$ , V/ $\text{TiO}_2\text{--Al}_2\text{O}_3$  and other catalysts by flame spray pyrolysis method. It was found that V was doped into the  $\text{Al}_2\text{O}_3$ -containing carrier with highly dispersed particles with the particle size of 5.8~9.4 nm. In  $\text{Al}_2\text{O}_3$ -non contained carrier, the particle size was



**Table 5 Catalytic reduction of NO<sub>x</sub> over vanadium-based catalysts**

Catalyst	Temperature/°C	NO concentration/ $\times 10^{-6}$ , vol	Conversion rate/%	Reference
7% V <sub>2</sub> O <sub>5</sub> /CVC-TiO <sub>2</sub>	250	200	96	[24]
7% V <sub>2</sub> O <sub>5</sub> /P25-TiO <sub>2</sub>	300	200	96	[24]
0.17V/TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	200	400	100	[25]
V/ZrO <sub>2</sub>	200	400	72	[26]

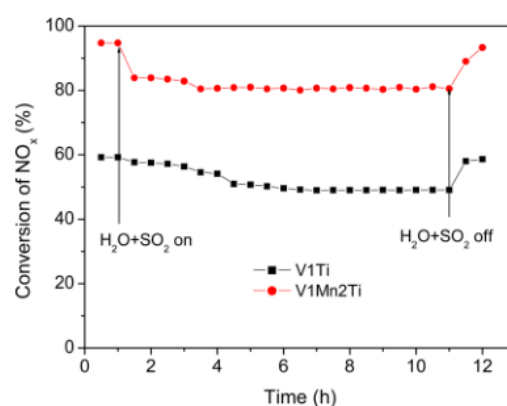
Fig.5 NO conversion with 5wt% and 7wt% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts using CVC-TiO<sub>2</sub> and P25-TiO<sub>2</sub> supports at different temperatures<sup>[20]</sup>

19~45.5 nm. The presence of Al<sub>2</sub>O<sub>3</sub> can greatly increase the amount of V<sup>3+</sup>, and TiO<sub>2</sub> can promote the formation of V<sup>4+</sup>, and both can promote the reaction of low temperature SCR. Boningari et al.<sup>[26]</sup> synthesized V/ZrO<sub>2</sub>, they found that when V/Zr atomic ratio was below 0.17, VO<sub>x</sub> mainly existed as a monomer and promoted catalytic reaction. When V/Zr atomic ratio was above 0.25, VO<sub>x</sub> mainly existed as polymerized species, and the SCR reaction was inhibited due to the lattice parameters change, crystal anisotropy, and the deficiency of active oxygen species. Jiang et al.<sup>[27]</sup> studied the effect of PbCl<sub>2</sub> on the V/TiO<sub>2</sub> catalyst, and found that 0.11% PbCl<sub>2</sub> can reduce the NO conversion rate by 50% in the temperature range of 200~300 °C, suggested the inactivation caused by Pb.

### 2.2.2 Bimetallic V–M catalysts

At present, catalysts have been widely used in commercial applications with V as active component. The V-based catalyst was doped with other metals to improve the low temperature activity of the catalyst. Chen et al.<sup>[28]</sup> reported the more vacancies caused by more Ce<sup>3+</sup> species promoted oxygen chemisorption and oxidation of more NO–NO<sub>2</sub>, and more tetrahedral WO<sub>x</sub> species caused by the interaction between Ce species and WO<sub>x</sub> species generated more Brønsted acid sites on the V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/CeO<sub>2</sub>–TiO<sub>2</sub> catalysts. Liu et al.<sup>[29]</sup> reported

the effects of H<sub>2</sub>O and SO<sub>2</sub> on the activities of VTi and VMn<sub>2</sub>Ti catalysts, and the results were showed in Fig.6. For both catalysts the coexistence of H<sub>2</sub>O and SO<sub>2</sub> led to the decrease of NO<sub>x</sub> conversion at 350 °C. However, the conversion over VMn<sub>2</sub>Ti was still much higher than that over VTi catalyst. After excluding H<sub>2</sub>O and SO<sub>2</sub> from the reactant feed, the NO<sub>x</sub> conversion was recovered over both catalysts.

Fig.6 Response of NO<sub>x</sub> conversion over VTi and VMn<sub>2</sub>Ti catalysts at 350 °C to intermittent feed of H<sub>2</sub>O and SO<sub>2</sub><sup>[29]</sup>

### 2.2.3 Summary of vanadium-based catalysts

The vanadium-based catalyst has good denitrification activity between 300~400 °C, which has good water and sulfur resistance. However, the general industrial flue gas denitration is arranged after dust removal and desulfurization, and its flue gas temperature is around 200 °C<sup>[30]</sup>. The vanadium-based catalyst has good water and sulfur resistance, but low temperature effect is poor<sup>[31]</sup>. Increasing the activity of the V-based catalyst in the low temperature range has great research value in practical industrial flue gas treatment<sup>[32]</sup>. Widening the temperature window of the V-based catalyst by doping the transition metal and from the aspects of preparation of the catalyst maybe can make the catalysts suitable for low temperature flue gas<sup>[33]</sup>. Water has a certain inhibitory effect on the catalyst. Since water occupies the acidic site of the catalyst surface, a small amount of NH<sub>3</sub> is adsorbed on the acidic site of the

catalyst. The catalyst activity is lowered by slowing down the SCR reaction.

### 2.3 Carbon-based Catalysts

Carbon-based materials are mainly activated carbon (AC), activated carbon fiber (ACF), and carbon nanotubes (CNTs), which were often used as catalyst supports because of their unique pore structure, large specific surface area, strong adsorption and chemical stability characteristics.

#### 2.3.1 Carbon materials supported catalysts

Some carbon-based catalyst in low temperature SCR reactions were summarized in Table 6. Li et al.<sup>[34,35]</sup> synthesized several  $\text{CuO}_x$  catalysts with different carbon-based supports by impregnation method. It was demonstrated that CNTs can promote the low temperature SCR reaction, and give wider reaction temperature range. It was believed that CNTs increased the amounts of acid sites on the catalyst surface and enhanced the reduction ability of the catalyst. The addition of Ce led to an increase of the amount of adsorbed oxygen, which further enhanced the activity of

the catalyst. Fan et al.<sup>[36]</sup> incorporated CNTs in  $\text{Mn-CeO}_x/\text{TiO}_2$  catalysts by sol-gel method, and the catalytic activity was improved. When the temperature was below 175 °C, CNTs had better NO adsorption ability. Zhang et al.<sup>[37]</sup> loaded  $\text{MnO}_x\text{-CeO}_x$  nanoparticles onto CNTs, and then coated with a mesoporous  $\text{TiO}_2$  to obtain a meso- $\text{TiO}_2@\text{MnO}_x\text{-CeO}_x/\text{CNT}$  composite catalyst with a core-shell structure. The migration and agglomeration of  $\text{MnO}_x\text{-CeO}_x$  particles improved the activity and stability of the catalyst. Zhang et al.<sup>[38]</sup> prepared  $\text{Mn-FeO}_x/\text{CNTs}$  by co-precipitation method, and the catalyst showed excellent low temperature SCR denitrification activity. XPS analysis demonstrated that a large amount of surface adsorbed oxygen existed on the catalyst surface and favored NO oxidation to  $\text{NO}_2$ , and the SCR reaction was accelerated. Huang et al.<sup>[39]</sup> loaded  $\text{V}_2\text{O}_5$  on MWCNTs. The effect of carbon nanotubes on denitrification was studied. The results showed that the denitrification efficiency was improved with the increase of nanotube diameter.

**Table 6 Catalytic reduction of  $\text{NO}_x$  over carbon-based catalysts**

Catalyst	Temperature/°C	NO concentration/ $\times 10^{-6}$ , vol	Conversion rate/%	Reference
6% $\text{CuO}_x\text{-CNTs}$	250	700	67	[34]
6% $\text{CuO}_x\text{-activated carbon}$	250	700	63	[34]
6% $\text{CuO}_x\text{-CuO}_x\text{-graphite}$	250	700	43	[34]
$\text{V}_2\text{O}_5/\text{TiO}_2\text{-CNTs}$	300	500	89	[35]
$\text{V}_2\text{O}_5\text{-CeO}_x/\text{TiO}_2\text{-CNTs}$	300	500	100	[36]
$\text{Mn-CeO}_x/\text{TiO}_2\text{-CNTs}$	125	1000	99.5	[37]
$\text{TiO}_2@\text{MnO}_x\text{-CeO}_x/\text{CNT}$	250	500	99	[38]
12% $\text{Mn-FeO}_x/\text{CNTs}$	140	500	100	[39]
2.35% $\text{V}_2\text{O}_5/\text{CNTs}$	190	800	92	[39]

#### 2.3.2 Summary of carbon-based catalysts

The carbon-based catalyst has a good low-temperature effect, doping modification of the transition metal enhances the denitration effect. However, there is poor water and sulfur resistance.  $\text{H}_2\text{O}$  and  $\text{SO}_2$  have large influence on the activity of the AC catalyst for NO reduction with  $\text{NH}_3$  at low temperatures. In the absence of  $\text{SO}_2$ , the inhibition effect of  $\text{H}_2\text{O}$  was small and possibly caused by competitive adsorption of  $\text{H}_2\text{O}$  and the reactants, such as  $\text{NH}_3$  and NO. The effect of  $\text{SO}_2$  was two-fold. In the absence of  $\text{H}_2\text{O}$ , the activity of AC catalyst increases with the addition of  $\text{SO}_2$ , in the presence of  $\text{H}_2\text{O}$ , however,  $\text{SO}_2$  deactivates the AC catalyst<sup>[40]</sup>. The deactivation of the AC catalyst in the

presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  is caused by the deposition of the ammonium sulfate salts on the catalyst surface. Higher  $\text{H}_2\text{O}$  content results in a higher deactivation rate of the catalyst<sup>[41]</sup>.

## 3 WATER AND SULFUR RESISTANCE IN LOW TEMPERATURE SCR REACTION

For low temperature SCR catalyst, the water and sulfur resistance determine the industrial application.  $\text{H}_2\text{O}$  and  $\text{SO}_2$  have an important effect on the denitrification efficiency of low temperature SCR catalyst, but the mechanism of action is different. The



effect of  $H_2O$  on the catalyst is divided into two types, the first one is  $H_2O$  and  $NO$ ,  $NH_3$  forming competitive adsorption and then reduced the active site. When  $H_2O$  is removed, the catalyst activity is recovered. Yu et al.<sup>[1]</sup> reported  $Mn-Ti-O$  catalysts were synthesized via solvothermal method. They find out that by depositing trace amount of  $SiO_2$  on  $Mn-Ti-O$  catalysts, the chemical properties (e.g., surface acidity, redox property, chemical valence) were barely changed, but the water tolerance was dramatically enhanced. Based on structural analysis, the pore sizes of catalysts were increased after  $SiO_2$  modification. Therefore, it is reasonable that the reduction of  $NH_3$ -SCR performances of catalysts in the presence of water highly related to the pore size of catalyst. This result may shed light on the design of  $NH_3$ -SCR catalysts with good water tolerance.  $NO$  conversion rate at  $150^\circ C$  over  $Mn_{0.2}Ti_{0.8}O_2$  declines to 60% after the addition of water vapor for 24 h. However, under the same condition,  $NO$  conversion rate at  $150^\circ C$  of  $SiO_2$ -modified samples still remained over 85% as shown in Fig.7<sup>[1]</sup>. They also illustrated the influence of water in Fig.8. At high temperature, water hardly condenses in the pore of catalyst. Hence,  $H_2O$  has limited influence on  $NH_3$ -SCR activities of catalysts. As the temperature decreases, water tends to condense in small pores of the catalyst because of the capillary effect. The condensed water blocks the pore and the active site of the catalyst, leading to the  $NH_3$ -SCR activity decrease. As the reaction temperature further declines, water seriously adsorbs on samples with varying average pore sizes.

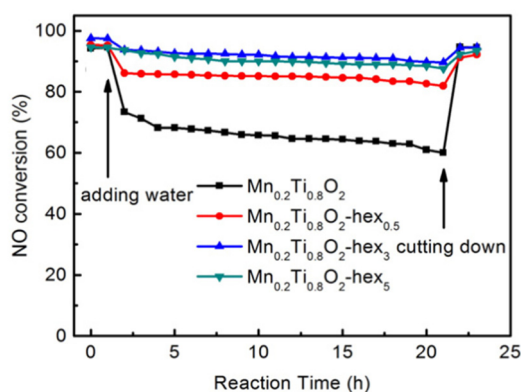


Fig.7 Water tolerances of catalysts<sup>[1]</sup>

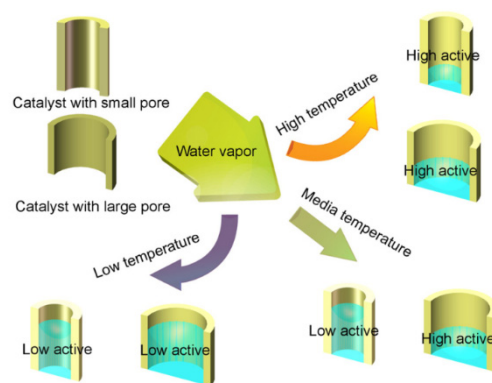


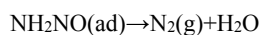
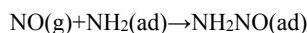
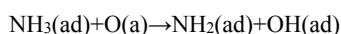
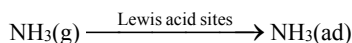
Fig.8 Illustration of the relationship among water tolerance at different temperatures, pore sizes, and capillarity<sup>[1]</sup>

Huang et al.<sup>[42]</sup> showed that the presence of  $H_2O$  did not reduce the adsorption of  $NO$  and  $NH_3$  at the Brewster acid site for the  $V_2O_5/AC$  catalyst, whereas the adsorption of  $NH_3$  on the catalyst surface increased. However, the  $NH_3$  activity adsorbed at the Lewis acid site significantly reduced, indicating that the SCR catalyst had a reduced denitration activity. The other was the chemical adsorption of  $H_2O$ .  $H_2O$  generated hydroxyl functional groups in the catalyst surface to caused deactivation of the catalyst, the activity cannot be recovered, leading to irreversible change even when  $H_2O$  was removed. For  $SO_2$  deactivation, one was the formation of ammonium sulfate adsorbed on the surface of the catalyst, which can't be decomposed at low temperatures, and thus accumulating on the catalyst surface, covering the active site, and decreasing the catalytic activity. The other was the formation of metal sulfates with active metal, and then resulting in an irreversible deactivation of the catalyst. Wu et al.<sup>[43]</sup> studied the Ce-doped  $Mn/TiO_2$  catalyst and found that the addition of Ce inhibited the formation of  $Ti(SO_4)_2$  and  $Mn(SO_4)_2$ , thereby improving the sulfur resistance of the catalyst.

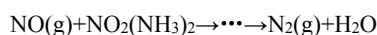
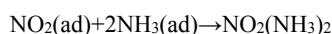
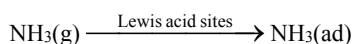
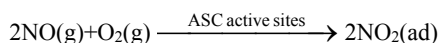
$H_2O$  and  $SO_2$  are usually present at the same time in industrial flue gas. How to improve water and sulfur resistance of the catalyst is a problem to be solved urgently for the low temperature SCR reaction. Replacement of sulfur-resistant catalyst carrier, such as carbon-based substances, adding additives, modifying the nanostructures of the catalysts, etc. are the possible solutions in the future research.

## 4 LOW TEMPERATURE SCR DENITRIFICATION MECHANISM

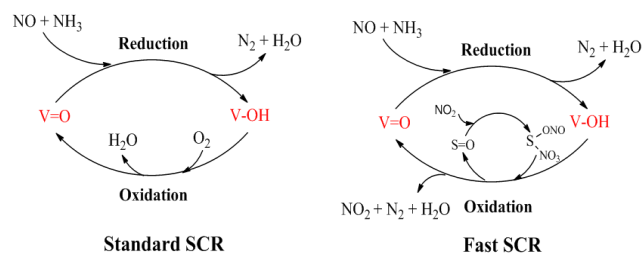
At present, it is generally believed that there are two kinds of low temperature SCR reaction paths. One is the Langmuir–Hinshelwood (L–H) mechanism<sup>[44]</sup>, that is, the reaction between  $\text{NH}_3$  and  $\text{NO}$  adsorbed on the catalyst, and finally decomposed into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The other is the Eley–Rideal (E–R) mechanism<sup>[45–47]</sup>, that is, the adsorption of  $\text{NH}_3$  and  $\text{NO}$  react to produce  $\text{N}_2$  and  $\text{H}_2\text{O}$ . In practice, the two paths usually occur at the same time. The denitrification mechanism is mainly L–H when the temperature is below  $150\text{ }^\circ\text{C}$ , and the reaction is mainly E–R mechanism<sup>[48,49]</sup> when the temperature is above  $150\text{ }^\circ\text{C}$ . Wang et al.<sup>[50]</sup> doped  $\text{CeO}_2$  into  $\text{Mn}/\text{ACH}$ , and found that the introduction of  $\text{CeO}_2$  promoted the oxidation of  $\text{NO}$  to  $\text{NO}_2$ , and further proceeded through the  $4\text{NH}_3+2\text{NO}+2\text{NO}_2\rightarrow 4\text{N}_2+6\text{H}_2\text{O}$  reaction. This reaction is 10 times faster than the standard SCR reaction  $4\text{NH}_3+4\text{NO}+\text{O}_2\rightarrow 4\text{N}_2+6\text{H}_2\text{O}$  and the denitrification efficiency was higher<sup>[51]</sup>. Tronconi et al.<sup>[52]</sup> found that  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$ , which is obtained by introducing  $\text{V}_2\text{O}_5$  into  $\text{WO}_3/\text{TiO}_2$  catalyst, also has a faster and more efficient rapid SCR reaction at  $250\text{ }^\circ\text{C}$ , and its reaction mechanism is shown in Fig.9<sup>[39]</sup>. Wang et al.<sup>[53]</sup> suggested that the low-temperature SCR reaction on the  $\text{V}_2\text{O}_5$  load active semi-coke (ASC), the two denitrification modes exist simultaneously. When the E–R path occurs, ASC is mainly used as the catalyst carrier, ASC mainly provides activity site adsorption of  $\text{NO}$  and  $\text{NH}_3$  when the L–H pathway occurred. The reaction equation is shown below:



Through the E–R mechanism path ASC mainly as a carrier:



The active site is mainly provided by the L–H mechanism path ASC.



(V=O and V–OH are oxidized and reduced vanadium sites, respectively, S=O is a non-reducible oxidic site)

Fig.9 Redox catalytic cycles of the standard and fast SCR reactions<sup>[39]</sup>

## 5 CONCLUSION AND PROSPECT

Nowadays, low temperature SCR denitrification technology has become a hot spot in the field of denitrification. From a large number of studies we can easily find that the current main problem is that the catalyst selectivity and stability are poor and weak in presence of water and sulfur at low temperatures. For the manganese-based catalyst, it has excellent activity, but poor resistance to water and sulfur. Vanadium-based catalyst has good resistance to water and sulfur, but low denitrification activity. Carbon-based catalyst contributed higher activity and resistance to water and sulfur, but the stability is not good enough. Further attention should be focused on above problems. Along with more stringent requirements for  $\text{NO}_x$  emissions, the iron ore sintering, coking, industrial boilers, glass and ceramic kilns, waste incineration, and petrochemical plants showed dramatic needs for low temperature SCR techniques.

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